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A Potential New RAFT-Click Reaction or a Cautionary Note on the Use of Diazomethane to Methylate RAFT-synthesized Polymers[†]

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It has been found that diazomethane undergoes a facile 1,3-dipolar cycloaddition with both dithiobenzoate RAFT agents and the dithiobenzoate end-groups of polymers formed by RAFT polymerization. Thus, 2-cyanoprop-2-yl dithiobenzoate on treatment with diazomethane at room temperature provided a mixture of stereoisomeric 1,3-dithiolanes in near quantitative (>95%) yield. A low-molecular-weight RAFT-synthesized poly(methyl methacrylate) with dithiobenzoate end-groups underwent similar reaction as indicated by immediate decolourization and a quantitative doubling of molecular-weight. Higher-molecular-weight poly(methyl methacrylate)s were also rapidly decolourized by diazomethane and provided a product with a bimodal molecular weight distribution. Under similar conditions, the trithiocarbonate group does not react with diazomethane.

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Introduction

Diazomethane is routinely used in polymer chemistry to methylate the carboxylic acid functionality in polymers or copolymers (e.g. those containing acrylic or methacrylic acid units^[1]). This treatment facilitates characterization by gel permeation chromatography (GPC) and NMR spectroscopy.

In recent years, reversible addition–fragmentation chain transfer (RAFT) polymerization, one of the most effective processes for reversible deactivation radical polymerization,^[2] has been successfully applied to a large range of monomers including those with unprotected carboxylic acid groups.^[3–8] The RAFT process involves performing a radical polymerization in the presence of certain thiocarbonylthio compounds (S=C(Z)–SR) known as RAFT agents. The RAFT agents provide living characteristics to the polymerization. The products of RAFT polymerization are themselves (macro-)RAFT agents and possess the S=C(Z)S– and R groups as chain ends (Scheme 1).

In an experiment where diazomethane was used to methylate RAFT-synthesized poly(methacrylic acid) with dithiobenzoate end groups, we observed, in addition to the expected methylation, that the (initially pink) polymer was decolourized and developed a bimodal molecular weight distribution with formation of a new peak with double the predicted molecular weight. This observation led us to examine the reaction of diazomethane

Monomer +
$$S \sim C \xrightarrow{S-R} Initiator \xrightarrow{R-P_x-S} C \xrightarrow{Z}$$

Scheme 1.

with the thiocarbonylthio end-group of RAFT-synthesized polymers in more detail.

The reaction between diazoalkanes and thiocarbonyl compounds was first reported in 1920 by Staudinger et al.^[9] who investigated the reaction between diphenyldiazomethane and various diaryl thioketones and commented that diphenyldiazomethane reacted only slowly with dithiobenzoates. Schönberg et al.^[10] extended this study to many diazoalkane–thiocarbonyl compound pairs. Depending on the reaction conditions and the specific reactants, 1,3-dithiolanes, thiiranes or alkenes were observed among the reaction products. However, the precise mechanism of the reaction remained unclear until Huisgen et al. isolated a thiadiazole intermediate (**2**) from the reaction of thiobenzophenone (**1**) and diazomethane at -78° C (Scheme 2).^[11]

It was proposed^[11] that diazomethane reacted with 1 in 1:1 stoichiometry at -78° C by 1,3-cycloaddition, producing the 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole (2). The thiadiazole 2 then eliminated N₂ in a 1,3-cycloreversion at -45° C, affording thiobenzophenone *S*-methylide (3). The reactive methylide 3 was not isolable but intercepted in situ by another molecule of 1 or a second dipolarophile, d=e, giving rise to the cycloadducts 4 or 5 respectively. Among the many dipolarophiles (e.g. C=S, C=O, C=C, and C≡C), thiocarbonyl compounds appeared to be more reactive toward 3, as evidenced by the formation of 1,3-dithiolane 4 in 95% yield even when 1 was treated with excess diazomethane at 20°C (the original conditions used by Schönberg). In competition with cycloaddition, or

[†]This paper is dedicated to the memory of Professor Athelstan L. J. Beckwith whose innovation and enthusiasm have inspired several generations of free radical chemists.



in the absence of intercepting reagents, the ylide **3** also underwent a head-to-head dimerization, to yield the 1,4-dithiane **6**, or irreversible electrocyclization to give the thiirane **7**. On heating or after extended reaction times, the latter (**7**) extruded sulfur to give 1,1-diphenylethylene (**8**). The mechanism for reactions between other thiocarbonyl compounds and diazo compounds (including that of diazomethane with dithioesters^[12–14]) was presumed to be analogous.

Results and Discussion

The Reaction of Diazomethane with Dithiobenzoates

When diazomethane was slowly introduced into a red solution of 2-cyanoprop-2-yl dithiobenzoate (9) in dichloromethane at 20°C, a brisk evolution of nitrogen was observed and the solution rapidly decolourized. Two 1,3-dithiolane stereoisomers, 10 and 11, were isolated from the reaction mixture by column chromatography in yields of 53 and 42% respectively. The proposed mechanism is shown in Scheme 3. The near-quantitative yield of 10 + 11 suggests that the reaction of 9 with the intermediate ylide 12 is substantially faster than the reaction of 9 with diazomethane. The identity of products was established by NMR spectroscopy. For the symmetrical *trans*-isomer 10, the 5-H₂ protons are identical, giving rise to a singlet signal at δ 4.51 in the ¹H NMR spectrum, whereas the spectrum of the *cis*-isomer 11 shows an AB pattern for the 5-H₂ protons at δ 3.91 and 4.62 with $J = 8.8 \,\text{Hz}$. Characterization of this compound by mass spectrometry posed a challenge, because the dithiolanes tend to fragment when ionized. The electron impact (EI) mass spectra showed only a weak molecular ion for the dithiolanes, in addition to several much more intense fragment ions.

The dithiolanes appear indefinitely stable at ambient temperature but isomerize, decompose or both on heating at elevated temperatures. For example, on heating in a melting point apparatus, an initially colourless sample of **10** was observed to turn red at $\sim 170^{\circ}$ C before meting at 180–181°C. Similarly, a sample of **11** was observed to turn red at $\sim 184^{\circ}$ C before melting at 188–189°C. Samples of pure **10** or **11** heated in [D5]chlorobenzene at >90°C in an NMR tube underwent isomerization to a mixture of **10** and **11** with noticeable reaction being observed after 30 min. At higher temperatures, conversion to **9** and unidentified by-products was observed, which may indicate that the formation of the dithiolanes is reversible. The dithiolane **10** was completely decomposed by heating at 105°C for 18 h.

The Reaction between Diazomethane and Polymers with Dithiobenzoate End-groups

A series of poly(methyl methacrylate) (PMMA) with narrow molecular weight distributions ($M_w/M_n < 1.2$) and average molecular weights (M_n) in the range ~2000–80000 were synthesized by RAFT polymerization using the dithiobenzoate RAFT agent 9. Treatment of dichloromethane solutions of these polymers with diazomethane at 20°C gave rapid decolourization. The molecular weight distributions of the isolated polymers were determined by GPC (Fig. 1). The chromatograms showed that the lowest-molecular-weight PMMA sample had quantitatively doubled in molecular weight. The highermolecular-weight PMMA samples each provided a product with a bimodal molecular weight distribution, with the formation of a higher-molecular-weight component approximately twice that of the original PMMA (Table 1, Fig. 1).

By analogy with the chemistry observed for 'small molecule' dithiobenzoates, we propose that the higher-molecular-weight component comprises PMMA chains joined by a 1,3-dithiolane linkage (15, Scheme 4). This structure results from 1,3-cycloaddition between ylide end-group 14 and the dithiobenzoate end-group 13. The fraction of the higher-molecular-weight component observed decreases with an increase in the molecular weight of the precursor PMMA. The proportion of this component (I_{mono}) was roughly estimated from a comparison of the corresponding GPC traces (Table 1).

One explanation for coupling not being quantitative is that the precursor polymer is contaminated by dead chains (i.e. without dithiobenzoate ends). Dead chains may be produced by termination or by irreversible chain transfer to initiator, solvent or monomer. If the initial RAFT agent is completely consumed, the number of dead chains formed by termination (D_c) should be approximately equal to the number of initiatorderived chains, and can be estimated using Eqn 1

$$D_{\rm c} = \frac{2df [\rm ACHN]_0 (1 - e^{-k_{\rm d}t})}{[\rm RAFT]_0 + 2df [\rm ACHN]_0 (1 - e^{-k_{\rm d}t})}$$
(1)

where *f* is the initiator efficiency (~0.5), *d* is the number of chains formed by radical–radical termination (2 for disproportionation, 1 for combination and ~1.67 for PMMA), *t* is time and k_d is the rate constant for initiator decomposition $(2.15 \times 10^{-5} \text{ s}^{-1} \text{ for } 1,1'\text{-azobis}(\text{cyclohexanecarbonitrile})$



Scheme 3.



Fig. 1. Molecular weight distributions of reversible addition–fragmentation chain transfer (RAFT)-synthesized poly(methyl methacrylate) before (—) and after (----) treatment with diazomethane.

(ACHN) at 90°C) (Table 1). The incidence of irreversible chain transfer should be negligible for the polymerization conditions used.

The finding that the fraction of uncoupled chains (I_{mono}) appears significantly greater than the estimated fraction of dead chains in the PMMA indicates that there must be another explanation.

A second explanation is that intramolecular electrocyclization of the polymeric ylide 14 to give thiirane 16 (Scheme 4) competes with intermolecular coupling between 13 and 14. The intramolecular electrocyclic ring closure becomes more competitive for higher-molecular-weight PMMA because the probability of the dithiobenzoate end-group 13 encountering the ylide 14 is reduced by the end-group concentration and the rate of end-group diffusion is lower (the solutions for the higher-molecular-weight polymers were also significantly more viscous).

Sasso et al.^[18] reported the diazomethane methylation of a RAFT-synthesized polymer. However, the dithiobenzoate ends had been previously removed by amine treatment and no unexpected reactions were reported.

The Reaction between Diazomethane and Trithiocarbonates

Similar experiments with diazomethane and either smallmolecule or polymeric trithiocarbonate compounds were performed using similar reaction conditions. The solution retained the yellow colour attributable to the trithiocarbonate chromophore and no change was detected by NMR. This is consistent with the trithiocarbonates being poorer dipolarophiles than dithiobenzoate.

A New RAFT-'Click' Reaction?

There has been recent interest in the direct transformation of RAFT end groups by the 'Click' reaction.^[19] One process investigated by Barner-Kowollik and coworkers^[20–28] is the hetero-Diels–Alder reaction with suitable dienes. It may be possible to make use of the chemistry described in the present paper to provide a method to functionalize polymers with dithiobenzoate ends. Mloston et al.^[12] have reported that the thiadiazole intermediates formed by reaction of phosphono-dithioformates with diazomethane are stable at -65° C and can be quantitatively converted to the ylide on warming to -35° C. This ylide could be trapped by various small molecule dipolarophiles.^[12]

The proposed process is shown in Scheme 5. The lowtemperature reaction with diazomethane forms the thiadiazole; the ylide can then be generated by warming the reaction mixture to react with a dipolarophile (A=B) (Scheme 5). This dipolarophile may be a RAFT agent or a macro-RAFT agent, providing a route to block copolymers.

The cycloaddition of RAFT agents (S=C(Z)–SR) with diazomethane is facilitated by electron-withdrawing Z and requires a dithiobenzoate (or more active RAFT agent). The hetero-Diels–Alder reaction examined by Barner-Kowollik and coworkers^[20–28] showed a similar but more pronounced trend. The reaction of the ylide is both more facile and less selective and, based on the work of Mloston et al.,^[12] a wide variety of dipolarophiles, including trithiocarbonates, can be used.

Conclusions

The interaction of diazomethane and thiocarbonylthio RAFT agents and macroRAFT agents has been studied. Diazomethane undergoes an extremely facile reaction with dithiobenzoates, though not with trithiocarbonates and, most likely, less active RAFT agents. This study suggests some limitations on the direct use of diazomethane to esterify polymers formed by RAFT

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Sample	$\textbf{9}\times 10^3~M$	Time [h]	Conversion [%]	$M_{\rm n}{}^{\rm A}$	M_n^{B}	$M_{\rm n}$ calc. ^C	$M_{\rm n} {\rm calc.}^{\rm D}$	$M_{\rm w}/M_{\rm n}$	$D_{\rm c}{}^{\rm E}$ [%]	<i>I</i> _{mono} ^F [%]
PMMA-1	181.0	16	46	2100	2300	1900	1900	1.16	1.2	_
PMMA-1-diazo	_	_	_	3500	3850	_		1.17	-	~ 0
PMMA-2	45.25	6	63	8900	9800	9300	8800	1.07	2.5	_
PMMA-2-diazo	_	_	_	14800	16200	_		1.12	-	25
PMMA-3	45.25	16	85	11800	13000	12500	12200	1.06	4.6	_
PMMA-3-diazo	_	_	_	19600	21500	_		1.12	-	21
PMMA-4	11.31	4	50	25900	28400	29200	23000	1.08	6.7	_
PMMA-4-diazo	_	_	_	36500	40000	_		1.16	-	38
PMMA-5	11.31	8	83	41000	44900	48300	40400	1.06	11.1	_
PMMA-5-diazo	_	_	_	58100	63600	_		1.14	_	38
PMMA-6	5.656	10	84	80400	88000	91900	73300	1.08	22.6	_
PMMA-6-diazo	_	-	-	104700	114500	-		1.17	-	48

 Table 1.
 The molecular weights of reversible addition-fragmentation chain transfer (RAFT)-synthesized poly(methyl methacrylate) (PMMA), the proportion of dead chains in that polymer, and the fraction of uncoupled chains after reaction with diazomethane

^AMolecular weight in polystyrene equivalents.

^BMolecular weight in PMMA equivalents from universal calibration with Mark–Houwink–Sakaruda parameters of $K = 11.4 \times 10^8 \text{ g L}^{-1}$, $\alpha = 0.716$ (PMMA),^[15] and $K = 9.44 \times 10^8 \text{ g L}^{-1}$, $\alpha = 0.719$ (polystyrene).^[16]

^CTheoretical molecular weights calculated using the expression

$$M_{\rm n} = \frac{[{\rm MMA}]_0 x}{[{\rm RAFT}]_0} M_{\rm MMA} + M_{\rm RAFT}$$

where x is the fractional monomer conversion, $[RAFT]_0$ and $[MMA]_0$ are the initial concentrations and M_{RAFT} and M_{MMA} the molecular weights of the initial RAFT agent and of MMA respectively.

^DTheoretical molecular weights calculated using the expression:^[4,17]

$$M_{\rm n} = \frac{[{\rm MMA}]_0 x}{[{\rm RAFT}]_0 + 2df [{\rm ACHN}]_0 (1 - e^{-k_d t})} M_{\rm MMA} + M_{\rm RAFT}$$

where *f* is the initiator efficiency (0.5), *d* is the number of chains formed by radical–radical termination (1.67 for PMMA) and k_d is the rate constant for initiator decomposition (2.15 × 10⁻⁵ s⁻¹ for 1,1'-azobis(cyclohexanecarbonitrile) (ACHN) at 90°C).

^EProportion of the dead chains D_c calculated using Eqn 1.

^FProportion of uncoupled chains I_{mono} based on relative intensity peaks in the gel permeation chromatograph (GPC) traces shown in Fig. 1 and the following assumptions: (a) the higher-molecular-weight peak is formed by coupling of two chains; (b) the peak intensity is proportional to the molecular weight.



polymerization with dithiobenzoate (or (macro)RAFT agents with similar or greater activity). Reaction of a polymer with trimethylsilyldiazomethane^[29] is likely to be subject to similar complications as those observed with direct treatment with diazomethane. Treatment of the polymer with methyl iodide and tetramethylammonium hydroxide^[30] may be complicated with conversion of the thiocarbonylthio end-group to a thiol end and subsequent formation of a coupled product by disulfide formation. It is recommended that the end-groups be removed from such RAFT-synthesized polymers before methylation. A variety of procedures are now available for this.^[19]

The present work also suggests a new 'Click' reaction for end-functionalizing RAFT-synthesized polymers by sequential treatment of a polymer with diazomethane (or other diazocompound) and a dipolarophile (A=B; Scheme 5). When the dipolarophile is a macro-RAFT agent, the product will be a block copolymer. This process will be the subject of future work.

Experimental Section

1,1'-Azobis(cyclohexanecarbonitrile) (Vazo88, DuPont) was used as received. Methyl methacrylate (MMA; Aldrich) was purified by vacuum distillation and then flash distilled before use. Solutions of diazomethane in diethyl ether^[31] and 2-cyanopropan-2-yl dithiobenzoate^[32] were prepared as reported previously (CAUTION! Diazomethane is toxic and potentially explosive. For safe handling procedures, see ref. [31]).

Scheme 5.

Melting points were obtained with an Electrothermal melting point apparatus and are uncorrected. Positive-ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using ionization energy of 70 eV. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer

(¹H, 400.13 MHz; ¹³C, 100.63 MHz) at 25°C in deuterated solvents as stated. Proton chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual protonated NMR solvent signal. Carbon chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the NMR solvent spectra.

Molecular weights of polymer were characterized by GPC performed in tetrahydrofuran (THF, 1.0 mL min⁻¹) at 30°C using a Waters GPC instrument with a Waters 2414 refractive index detector, a series of four Polymer Laboratories PLGel columns ($3 \times 5 \mu$ m Mixed-C and $1 \times 3 \mu$ m Mixed-E) and *Empower* software. The GPC was calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories Easi-Cal, molecular weight from 264 to 256000). PMMA molecular weights are based on application of universal calibration and Mark–Houwink–Sakaruda parameters of $K = 11.4 \times 10^8 \text{ g L}^{-1}$, $\alpha = 0.716$ (PMMA),^[15] and $K = 9.44 \times 10^8 \text{ g L}^{-1}$, $\alpha = 0.719$ (polystyrene).^[16]

Synthesis of 1,3-Dithiolane 10 and 11. An ethereal solution of diazomethane was added dropwise to a dichloromethane solution (2 mL) of the dithiobenzoate 9 (221 mg, 1.00 mmol) at 20°C until the red colour of the reaction mixture had vanished. The solution was evaporated to dryness, and purified by column chromatography on silica gel (Kieselgel-60, 230–400 mesh) with ethyl acetate/*n*-hexane 10:90 (v/v) as eluent to afford the two stereoisomers of the 1,3-dithiolane, 10 (121 mg, 53%) and 11 (96 mg, 42%). Both products were recrystallized from a mixture of dichloromethane and methanol.

10. Mp: 180–181°C. $\delta_{\rm H}$ (400.13 MHz, C₆D₅Cl) 0.93 (s, 6H), 1.23 (s, 6H), 4.51 (s, 2H), 7.08–7.16 (m, 6H), 7.80 (bs, 4H). $\delta_{\rm C}$ (100.63 MHz, C₆D₅Cl) 27.60, 28.89, 30.98, 39.88, 85.45, 123.86, 125.82, 126.02, 127.29, 128.10, 128.30, 129.12, 129.32, 131.93, 135.32. *m/z* (EI-MS) 456.1 (2, M⁺), 388.0 (12), 356.1 (14), 256.0 (100), 210.0 (29), 167.0 (24), 121.0 (80), 77.0 (15).

11. Mp: 188–189°C. $\delta_{\rm H}$ (400.13 MHz, C₆D₅Cl) 1.00 (s, 6H), 1.34 (s, 6H), 3.91 (d, 1H, *J* 8.8), 4.62 (d, 1H, *J* 8.8), 6.88–6.94 (m, 4H), 6.99–7.04 (m, 2H), 7.36 (bd, 4H, *J* 7.7). $\delta_{\rm C}$ (100.63 MHz, C₆D₅Cl) 28.08, 29.39, 33.30, 39.97, 85.33, 123.03, 125.83, 126.03, 126.97, 128.10, 128.30, 128.60, 129.13, 129.32, 130.94, 137.97. *m/z* (EI-MS) 456.1 (2, M⁺), 388.1 (16), 356.1 (8), 256.1 (85), 210.1 (23), 167.0 (28), 121.0 (100), 77.1 (20).

Synthesis of PMMA by RAFT Polymerization

Solutions of 9, ACHN (4.5 mg, 1.84×10^{-3} M), MMA (6.552 g, 6.552 M) in benzene (3 mL) were transferred to an ampoule which was degassed through three freeze–pump–thaw cycles, sealed under vacuum, and heated at 90°C for the stated time. The polymers were then precipitated twice into *n*-hexane (100 mL), filtered, and washed with *n*-hexane (50 mL) to give the polymers. The polymerization conditions and conversions are summarized in Table 1.

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References

- A. Katchalsky, H. Eisenberg, J. Polym. Sci., Polym. Phys. Ed. 1951, 6, 145. doi:10.1002/POL.1951.120060202
- [2] A. D. Jenkins, R. I. Jones, G. Moad, Pure Appl. Chem. 2010, 82, 483. doi:10.1351/PAC-REP-08-04-03

- [3] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* 1998, 31, 5559. doi:10.1021/MA9804951
- [4] G. Moad, E. Rizzardo, S. H. Thang, Aust. J. Chem. 2005, 58, 379. doi:10.1071/CH05072
- [5] G. Moad, E. Rizzardo, S. H. Thang, Aust. J. Chem. 2006, 59, 669. doi:10.1071/CH06250
- [6] G. Moad, E. Rizzardo, S. H. Thang, Acc. Chem. Res. 2008, 41, 1133. doi:10.1021/AR800075N
- [7] G. Moad, E. Rizzardo, S. H. Thang, *Polymer* 2008, 49, 1079. doi:10.1016/J.POLYMER.2007.11.020
- [8] G. Moad, E. Rizzardo, S. H. Thang, Aust. J. Chem. 2009, 62, 1402. doi:10.1071/CH09311
- [9] H. Staudinger, J. Siegwart, *Helv. Chim. Acta* 1920, 3, 833. doi:10.1002/ HLCA.19200030178
- [10] A. Schönberg, B. Koenig, E. Singer, Chem. Ber. 1967, 100, 767. doi:10.1002/CBER.19671000310
- [11] R. Huisgen, I. Kalvinsch, X. Li, G. Mloston, Eur. J. Org. Chem. 2000, 2000, 1685.
- [12] G. Mloston, K. Urbaniak, M. Gulea, S. Masson, A. Linden, H. Heimgartner, *Helv. Chim. Acta* 2005, 88, 2582. doi:10.1002/HLCA. 200590198
- [13] J. M. Beiner, D. Lecadet, D. Paquer, A. Thuillier, J. Vialle, Bull. Soc. Chim. Fr. 1973, 1979.
- [14] G. Mloston, J. Romanski, E. B. Rusanov, A. N. Chernega, Y. G. Shermolovich, Zh. Org. Khim. 1995, 31, 1027.
- [15] R. A. Hutchinson, J. H. McMinn, D. A. Paquet, S. Beuermann, C. Jackson, *Ind. Eng. Chem. Res.* **1997**, *36*, 1103. doi:10.1021/ IE9604031
- [16] R. A. Hutchinson, S. Beuermann, D. A. Paquet, Jr, J. H. McMinn, *Macromolecules* **1997**, *30*, 3490. doi:10.1021/MA970176U
- [17] Y. K. Chong, G. Moad, E. Rizzardo, M. A. Skidmore, S. H. Thang, *Macromolecules* 2007, 40, 9262. doi:10.1021/MA071100T
- [18] B. Sasso, M. Dobinson, P. Hodge, T. Wear, *Macromolecules* 2010, 43, 7453. doi:10.1021/MA1011683
- [19] G. Moad, E. Rizzardo, S. H. Thang, Polym. Int. 2011, 60, 9. doi:10.1002/PI.2988
- [20] A. J. Inglis, S. Sinnwell, T. P. Davis, C. Barner-Kowollik, M. H. Stenzel, *Macromolecules* 2008, 41, 4120. doi:10.1021/MA8002328
- [21] S. Sinnwell, A. J. Inglis, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Chem. Commun.* 2008, 2052. doi:10.1039/B718180A
- [22] S. Sinnwell, C. V. Synatschke, T. Junkers, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* 2008, 41, 7904. doi:10.1021/MA8013959
- [23] S. Sinnwell, M. Lammens, M. H. Stenzel, F. E. Du Prez, C. Barner-Kowollik, J. Polym. Sci. A Polym. Chem. 2009, 47, 2207. doi:10.1002/ POLA.23299
- [24] S. Sinnwell, A. J. Inglis, M. H. Stenzel, C. Barner-Kowollik, *Macromol. Rapid Commun.* 2008, 29, 1090. doi:10.1002/MARC. 200800233
- [25] L. Nebhani, S. Sinnwell, A. J. Inglis, M. H. Stenzel, C. Barner-Kowollik, L. Barner, *Macromol. Rapid Commun.* 2008, 29, 1431. doi:10.1002/MARC.200800244
- [26] A. J. Inglis, S. Sinnwell, M. H. Stenzel, C. Barner-Kowollik, Angew. Chem. Int. Ed. Engl. 2009, 48, 2411. doi:10.1002/ANIE.200805993
- [27] L. Nebhani, P. Gerstel, P. Atanasova, M. Bruns, C. Barner-Kowollik, J. Polym. Sci. A Polym. Chem. 2009, 47, 7090. doi:10.1002/POLA.23756
- [28] L. Nebhani, S. Sinnwell, C. Y. Lin, M. L. Coote, M. H. Stenzel, C. Barner-Kowollik, J. Polym. Sci. A Polym. Chem. 2009, 47, 6053. doi:10.1002/POLA.23647
- [29] L. Couvreur, C. Lefay, J. Belleney, B. Charleux, O. Guerret, S. Magnet, *Macromolecules* 2003, *36*, 8260. doi:10.1021/MA035043P
- [30] L. Hutson, J. Krstina, C. L. Moad, G. Moad, G. R. Morrow, A. Postma, E. Rizzardo, S. H. Thang, *Macromolecules* 2004, 37, 4441. doi:10.1021/ MA049813O
- [31] F. Arndt, in Organic Synthesis (Collective Vol. 2) (Ed. A. H. Blatt) 1943, pp. 165–167 (Wiley: New York).
- [32] S. H. Thang, Y. K. Chong, R. T. A. Mayadunne, G. Moad, E. Rizzardo, *Tetrahedron Lett.* **1999**, 40, 2435. doi:10.1016/S0040-4039(99)00177-X

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